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(54) METHOD FOR PRETREATMENT OF MOLTEN IRON AND METHOD FOR REFINING

VERFAHREN ZUR VORBEHANDLUNG VON SCHMELZFLÜSSIGEM EISEN UND FEINUNGSVERFAHREN

PROCEDE DE PRETRAITEMENT DE FER FONDU ET PROCEDE DE RAFFINAGE

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- **PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) -& JP 09 020914 A (NIPPON STEEL CORP), 21 January 1997 (1997-01-21)**
- **KISHIDA T ET AL: "CONSTRUCTION AND OPERATION OF HOT METAL DEPHOSPHORIZATION PLANT AT THE WAKAYAMA STEEL WORKS" SUMITOMO SEARCH, SUMITOMO METAL INDUSTRIES, TOKYO, JP, vol. 33, November 1986 (1986-11), pages 9-15, XP009010700 ISSN: 0585-9131**
- **PATENT ABSTRACTS OF JAPAN vol. 012, no. 015 (C-469), 16 January 1988 (1988-01-16) & JP 62 170409 A (KOBE STEEL LTD), 27 July 1987 (1987-07-27)**

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Description

Technical Field

[0001] The present invention relates: to a molten iron pretreatment method wherein molten iron is desiliconized and dephosphorized in a refining vessel capable of top and bottom blowing; and to a molten iron refining method wherein molten iron is decarburized after said molten iron pretreatment.

Background Art

[0002] A molten iron pretreatment method wherein molten iron is desiliconized and dephosphorized in another vessel different from a vessel in which the molten iron is subsequently decarburized has been employed in place of a converter steelmaking method wherein molten iron is simultaneously desiliconized, dephosphorized and decarburized in a converter. In molten iron pretreatment at an early stage, it has been the common method to refine molten iron by adding a solid oxygen source including iron oxide and desiliconizing the molten iron and subsequently adding a flux for dephosphorization and dephosphorizing the molten iron. In the dephosphorization refining, molten iron has been dephosphorized by adding a lime source as a flux, thus forming dephosphorizing slag having a high basicity, and further adding a solid oxygen source including iron oxide as another flux. As a vessel for preliminary dephosphorization refining, a torpedo car or a ladle has been used and a method wherein molten iron is dephosphorized preliminarily by injecting a flux for dephosphorization into the molten iron in the vessel has been employed. Here, solid oxygen means oxygen contained in iron oxide (FeO, Fe_2O_3) and a solid oxygen source means a substance containing iron oxide such as iron ore, dust and mill scale, these being used as a flux or a coolant.

[0003] Recently, a molten iron pretreatment method wherein a converter-type refining vessel capable of top and bottom blowing is employed as a molten iron pretreatment vessel and molten iron is desiliconized and dephosphorized simultaneously has been adopted. In this method, as the dephosphorization can be accelerated by the strong stirring caused by the top and bottom blowing even when slag having a low basicity is used, it is possible to simultaneously desiliconize and dephosphorize molten iron. Further, as enough oxygen gas can be used as an oxygen source, a molten iron temperature after pretreatment can be maintained at a high temperature in comparison with a conventional method wherein only solid oxygen is used or, even when oxygen gas is used, a very small amount of that is used, and moreover, since the treatment time can be shortened, in comparison with a pretreatment wherein a torpedo car is used, the heat loss during the pretreatment is small and a heat margin in all the refining processes including a decarburization treatment process can be secured. As a method of adding a flux for pretreatment refining to molten iron, a method wherein a flux is added to molten iron in a refining vessel from above or an injection method wherein a flux is added to molten iron by injecting bottom-blown gas into the molten iron as the carrier gas of the flux can be adopted. By adopting the flux injection method, it is possible to improve the dephosphorization efficiency in pretreatment.

[0004] In the dephosphorization of molten iron, the dephosphorizing capability increases as a molten iron temperature, at the end of pretreatment, lowers. Therefore, despite the fact that a heat margin can be increased by using gas oxygen in pretreatment, an excessive rise of a molten iron temperature after pretreatment makes it impossible to sufficiently exploit the dephosphorizing capability in a pretreatment.

[0005] In the desiliconization and dephosphorization of molten iron, as the molten iron is refined by adding an oxygen source, carbon in the molten iron is unavoidably oxidized and, thus, decarburization advances and this causes heat margin at the time of decarburization treatment to be lost.

[0006] If a carbon source is added to molten iron during molten iron pretreatment or decarburization refining, the carbon source is used as a heat source during decarburization treatment and resultantly the heat margin in refining can be increased. As a method of adding a carbon source during decarburization treatment, a method wherein lump anthracite is added from above may be adopted. However, the problem of the method is that the dispersion loss of carbon caused by the upward flow of gas generated by oxygen top blowing is large. Further, since SiO_2 included in carbonaceous materials is added to molten iron, an increase in the burnt lime is undesirably required for securing the basicity of slag during decarburization treatment.

[0007] As a method of adding a carbon source to molten iron during molten iron pretreatment for desiliconization and dephosphorization, Japanese Unexamined Patent Publication No. S62-170409 discloses a method comprising the processes of: adding from above a flux produced by combining main component SiO_2 with a slag formation improvement material (Mn ore, calcium fluoride (fluorite), etc.) at the first stage of molten iron pretreatment; injecting a flux for desiliconization (iron oxide) into the molten iron; supplying a gas/solid oxygen source to the surface of the molten iron; simultaneously injecting a carbon source with a carrier gas into the molten iron together with the injection of the flux for desiliconization or after the completion of desiliconizing reaction; and resultantly increasing the concentration of carbon in the molten iron. It is said that the reason for adding a CaO-based flux from above is that, if a CaO-based flux containing iron oxide used for dephosphorization is injected into molten iron together with a carbon source, the oxygen potential in the molten iron lowers because of the injection of carbon and the dephosphorizing reaction is hindered.

[0008] When using fluorite in refining, the refractories of a refining vessel used for pretreatment or decarburization treatment are eroded severely. As shown in Fig 6 of Japanese Unexamined Patent Publication No. H8-157921 for example, it is known that a refractory erosion index increases and the refractory erosion also increases radically as a fluorine concentration in slag increases. Therefore, it is preferable not to use fluorite from the viewpoint of the service life extension of refractories.

[0009] In the invention disclosed in the aforementioned Japanese Unexamined Patent Publication No. S62-170409 wherein a carbon source is injected into molten iron during molten iron pretreatment, as a flux is added from above, a slag formation improvement material such as calcium fluoride (fluorite) must be inevitably added for securing the fluidity of slag and therefore the method undesirably goes against the aforementioned trend of not using fluorite. Here, if fluorite is not used during pretreatment, the dephosphorizing capability in pretreatment is insufficient and it becomes necessary to form slag for dephosphorization by using fluorite and to dephosphorize molten iron in the subsequent decarburization treatment. Further refinement processes are disclosed for example in JP0920914A. In molten iron refining processes comprising the steps of applying molten iron pretreatment wherein molten iron is desiliconized and dephosphorized in single vessel without intermediate slag discharging and subsequently applying decarburization refining, a conventional molten iron pretreatment has difficulty in sufficiently dephosphorizing molten iron after the pretreatment and therefore it has been required to form slag and dephosphorize molten iron even in decarburization treatment. The formation of slag for dephosphorization in a decarburization process causes the cost to increase and further makes it necessary to use fluorite for the formation of slag for dephosphorization in a decarburization process and therefore the method goes against the aforementioned trend of not using fluorite.

[0010] The object of the present invention is to provide a pretreatment method and a refining method for molten iron, the methods allowing the refining to not use fluorite in both the processes of molten iron pretreatment and decarburization, to minimize the formation of slag for dephosphorization in the decarburization process, and to increase a heat margin by adding a carbon source to the molten iron with great efficiency.

Disclosure of the Invention

[0011] During a desiliconizing reaction period in the first stage of molten iron pretreatment, using a conventional method wherein iron oxide is mainly injected as an oxygen source for desiliconization into molten iron together with a carrier gas, a molten iron temperature does not rise sufficiently at the desiliconizing reaction period and the formation of slag for dephosphorization refining becomes insufficient. In contrast, when oxygen gas is used as an oxygen source for desiliconization, a molten iron temperature rises conspicuously at the desiliconizing reaction period, slag for dephosphorization refining is formed sufficiently, and resultantly the dephosphorizing reaction advances with great efficiency.

[0012] By using mainly top-blown oxygen gas as an oxygen source for desiliconization, the amount of a flux injected into molten iron during a desiliconizing reaction period can considerably be reduced. Therefore, if a carbon source is injected into molten iron as a heat source together with a carrier gas at a desiliconizing reaction period, it becomes possible to add only a carbon source to molten iron before the commencement of flux injection. In this case, the carbon source and a flux containing lime-based components for dephosphorization are not injected at the same time and therefore the hindrance of dephosphorization by the injection of a carbon source is avoided. Further, by eliminating the simultaneous injection of a carbon source and an iron oxide-contained flux, the effect of avoiding the risk of reaction between the carbon source and the iron oxide, and the resultant ignition, can be achieved.

[0013] Accordingly, it has been clarified that the extensive improvement of the dephosphorization efficiency in molten iron pretreatment and the increase of heat margin in all the refining processes can be achieved by using mainly top-blown gas oxygen as an oxygen source for desiliconization and simultaneously injecting a carbon source into molten iron as the heat source during a desiliconizing reaction period.

[0014] The present invention has been established on the basis of the above findings and the gist of the present invention is as set forth in claim 1, as follows:

> (1) A molten iron pretreatment method wherein molten iron is desiliconized and dephosphorized by using a refining vessel capable of top and bottom blowing and injecting a flux mainly composed of a component consisting of one or more of burnt lime, limestone and iron oxide, the component containing at least iron oxide, into the molten iron, characterized by injecting a carbon source into the molten iron during desiliconizing reaction and starting the carbon source injection prior to the commencement of said flux injection, wherein oxygen gas is blown into the molten iron and the carbon source is injected through a bottom nozzle and the desiliconization step takes place using the top blown oxygen gas.
>
> (2) A molten iron pretreatment method according to the item (1), characterized by starting said flux injection after an [Si] concentration is lowered to 0.15 mass %.

(3) A molten iron pretreatment method according to the item (1) or (2), characterized by starting said flux injection after the completion of the carbon source injection.

(4) A molten iron pretreatment method according to any one of the items (1) to (3), characterized by not using fluorite during the molten iron pretreatment.

(5) A molten iron refining method wherein molten iron is subjected to decarburization treatment after subjected to molten iron pretreatment by the molten iron pretreatment method according to any one of the items (1) to (4), characterized by not using fluorite during said decarburization treatment.

Brief Description of the Drawings

[0015] Figure 1 is a schematic illustration showing a molten iron pretreatment furnace used in the present invention.

Best Mode for Carrying Out the Invention

[0016] In molten iron pretreatment according to the present invention, a refining vessel 1 capable of top and bottom blowing is used as shown in Figure 1. In top blowing, mainly oxygen gas 8 is blown from the tip of a top-blowing lance 3 onto the surface of molten iron. A top-blown oxygen gas used during a desiliconizing reaction period may be used as an oxygen source for desiliconization. In a dephosphorizing reaction period, the top blowing is used not only for preventing the restoration of phosphorus by raising the oxygen potential of slag but also for controlling a molten iron temperature to a prescribed temperature by making up for heat dissipation.

[0017] In bottom blowing, bottom-blowing nozzles 2 disposed at the bottom of the refining vessel 1 are used. The bottom blowing has the functions of: stirring molten iron by injecting a gas containing oxygen gas or an inert gas through the nozzles; and injecting fluxes 9 together with a carrier gas 7 into the molten iron through the bottom-blowing nozzles 2.

[0018] By using two top- and bottom-blown converters, it is possible to use one of them for molten iron pretreatment and the other for decarburization treatment. Molten iron is subjected to pretreatment in a converter for molten iron pretreatment, subsequently transferred to the other converter for decarburization treatment, and subjected to decarburization treatment.

[0019] In molten iron pretreatment according to the present invention, a flux injected together with a carrier gas into molten iron is mainly composed of a component consisting of one or more of burnt lime, limestone and iron oxide, the component containing at least iron oxide. A flux used for dephosphorization contains iron oxide and a CaO source such as burnt lime and limestone. A flux mainly composed of iron oxide may be injected as a desiliconization aid prior to the commencement of the injection of a flux for dephosphorization. Iron ore, mill scale, sinter dust and other various sources may be adopted as iron oxide used as a flux component.

[0020] During the desiliconizing reaction in molten iron pretreatment, a top-blown gas oxygen is mainly used as an oxygen source. A flux containing iron oxide may be injected into molten iron together with a carrier gas during desiliconizing reaction and used as an oxygen source aid for desiliconization. However, even in this case, at the first stage of desiliconization, only the gas oxygen should be used as the oxygen source for desiliconization and a flux for desiliconization should not be injected.

[0021] A carbon source is injected together with a carrier gas through bottom-blowing nozzles into molten iron during desiliconizing reaction in molten iron pretreatment. Anthracite powder, coke powder and others may be used as a carbon source. Carbon source injection is started prior to the commencement of the aforementioned flux injection. Therefore, there is always a time period during which the aforementioned flux injection is not applied but the carbon source injection is applied. As a carbon source alone is injected, such a problem of hindering dephosphorization as seen in the case of simultaneously injecting a carbon source and a flux for dephosphorization is avoided.

[0022] In the present invention, as a desiliconizing reaction is advanced not by a solid oxygen source that has been traditionally used but mainly by top-blown gas oxygen, it is possible to maintain a molten iron temperature, higher than before, during and after the desiliconizing reaction. As a result, the slag formation of injected flux can be accelerated and the dephosphorizing reaction can also be accelerated conspicuously during molten iron pretreatment.

[0023] Here, the term "during desiliconizing reaction" means the time period during which an [Si] concentration is being lowered with the lapse of time by the oxidation of [Si] in molten iron. In general, when an [Si] concentration in molten iron lowers to 0.03 mass %, an oxidizing velocity of [Si] decreases considerably and, therefore, a desiliconizing reaction is regarded as completed.

[0024] As long as carbon source injection is started prior to the commencement of flux injection, the flux injection may be started at any time during desiliconizing reaction. Unless flux injection is started at least at the end of desiliconizing reaction, a dephosphorizing reaction succeeding the desiliconizing reaction cannot be processed smoothly. In the meantime, as shown in the aforementioned item (2) of the present invention, it is preferable to start flux injection after an [Si] concentration is lowered to 0.15 mass %. After an [Si] concentration is lowered to 0.15 mass %, if dephosphorizing slag (flux) exists, dephosphorizing reaction advances together with desiliconizing reaction. Therefore, by starting flux injection after an [Si] concentration is lowered to 0.15 mass %, dephosphorizing reaction can be accelerated effectively during desiliconizing reaction. A desirable means for determining an [Si] concentration during desiliconization is to estimate a desiliconized amount from an oxygen supply amount and a desiliconizing reaction efficiency on the basis of an initial value of [Si] in molten iron.

[0025] In a desiliconizing reaction period, the effect of the present invention can be achieved even though a time period at which a carbon source and a flux are injected simultaneously exists. However, by starting flux injection after the completion of carbon source injection as described in the aforementioned item (3) of the present invention, it is desirably possible to avoid not only the inefficiency of a dephosphorizing flux caused by the simultaneous injection of a flux for dephosphorization and a carbon source but also a risk of ignition as seen in the case of simultaneously injecting a carbon source and a flux containing iron oxide.

[0026] In the present invention, since desiliconization is advanced by using top-blown gas oxygen, a molten iron temperature after desiliconizing reaction is high, the formation of dephosphorizing slag is satisfactory, and resultantly succeeding dephosporizing reaction advances smoothly. At the same time, since a carbon source is injected, it is possible to increase a heat margin during refining and resultantly to lower a molten iron temperature at the end of dephosphorization after a molten iron pretreatment. By lowering a molten iron temperature at the end of dephosphorization, it is possible to prevent the restoration of phosphorus and, as a result, to improve dephosphorizing capability. As the present invention favors dephosphorization in molten iron pretreatment in this way, it becomes possible to advance a prescribed dephosphorizing reaction without the use of fluorite in a molten iron pretreatment as described in the aforementioned item (4) of the present invention.

[0027] In the present invention, as a dephosphorizing capability is excellent in a molten iron pretreatment, it is not necessary to apply an additional dephosphorization treatment during decarburization treatment. Therefore, it becomes possible to lower a phosphorus concentration in molten steel to a prescribed concentration without the use of fluorite during decarburization treatment as described in the aforementioned item (5) of the present invention.

[0028] In the present invention, as heat margin at refining is increased by adding a carbon source during molten iron pretreatment, it becomes possible to raise a charge ratio of a coolant iron source such as scrap and to add Mn ore instead of expensive Mn ferroalloy in decarburization treatment. Further, since the formation of dephosphorizing slag is not required and the amount of slag is small in a decarburization treatment, it becomes possible to improve the Mn yield of Mn ore.

Examples

[0029] High-carbon low-phosphorus steels were melted and refined by using two 280-ton top- and bottom-blown converters; one as a refining vessel 1 for molten iron pretreatment as shown in Figure 1 and the other as a refining vessel for decarburization treatment.

[0030] Top blowing was carried out by using a top-blowing lance 3 and blowing oxygen gas 8 onto molten iron 5. Bottom blowing was carried out by using six dual-tube bottom-blowing nozzles 2 and injecting oxygen gas or an inert gas into molten iron through the inner tubes. Through the space between the inner tube and the outer tube of each lance, a hydrocarbon gas was injected as a cooling gas during the oxygen gas injection through the inner tubes and an inert gas such as a nitrogen gas was injected during the inert gas injection through the inner tubes. In the molten iron pretreatment furnace, fluxes 9 stored in flux hoppers 4 could be injected together with a carrier gas 7 through bottom-blowing tuyeres 2. A carbon source 9c, burnt lime 9a and sinter dust 9b were used as the fluxes 9. In this case, an inert gas was used as the carrier gas 7.

[0031] As the carbon source 9c injected together with the carrier gas 7 through the bottom-blowing tuyeres, anthracite containing 80 mass % FC (Fixed Carbon; fixed carbon in coal), 6 mass % VM (Volatile Matter; volatile matter in coal) and 6.7 mass % SiO_2 was used. Further, as a flux injected likewise, a mixture of the burnt lime powder 9a and the sinter dust 9b blended at the ratio of 1 to 1 in mass or the sinter dust 9b alone was used. The composition of the sinter dust was, in mass, 46.7% T. Fe (total Fe), 6% CaO, 2.5% Al_2O_3 and 5.2% SiO_2. The grain size of each of the injected materials was adjusted to 1.5 mm or less. The flow rate of top blowing during a dephosphorizing reaction period was determined so as to not only prevent the restoration of phosphorus by increasing the oxygen potential of slag 6 but also control a molten iron temperature to a prescribed temperature by making up for heat dissipation.

[0032] Table 1 shows mainly the carbon source in pretreatment and the flux injection state of each example. Table 2 shows the detailed results of the unit consumptions, the components and the temperatures of each example. The invention examples 1 and 2 are the cases where the present invention is applied and the comparative examples 1 to 4 are the cases where prior arts are applied.

[Table 1]

	Pretreatment furnace			Decarbrization furnace
	Desiliconization period	Dephosphorization period	End temperature	
Invention example 1	Powder carbon injection	CaO + sinter dust injection	Ordinary	No carbonaceous material addition
Invention example 2	Powder carbon injection up to 0.15% [Si] CaO	+ sinter dust injection after 0.15% [Si]	Ordinary	No carbonaceous material addition
Comparative example 1	Powder carbon + sinter dust injection	CaO + sinter dust injection	Ordinary	No carbonaceous material addition
Comparative example 2	Sinter dust injection	CaO + sinter dust injection	Ordinary	Carbonaceous material added (added from above in blocks)
Comparative example 3	No flux injection	No flux injection	Ordinary	No carbonaceous material addition
Comparative example 4	No flux injection	No flux injection	End temperature rise	No carbonaceous material addition

[Table 2]

		Invention example 1	Invention example 2	Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4
Pretreatment furnace	Molten iron amount (t/ch)	282	279	280	283	280	278
	Initial temperature (°C)	1301	1302	1299	1300	1300	1301
	Initial [C] (mass %)	4.59	4.61	4.62	4.63	4.59	4.58
	Initial [P] (mass %)	0.101	0.102	0.100	0.102	0.100	0.101
	Powder carbon unit consumption (kg/t)	7.1	3.6	7.1	0	0	0
	Powder carbon injection time (min.)	4	2	4	-	-	-
	CaO + sinter dust unit consumption (kg/t)	17.8	17.8	17.8	17.8	0	0
	CaO upward charge unit consumption (kg/t)	5.9	5.9	5.9	5.9	13.9	13.9
	Top-blown oxygen unit consumption (Nm^3/t)	15.8	15.8	15.0	15.0	17.0	17.0
	Total treatment time (min.)	14	14	14	14	14	14
	Temperature after treatment (°C)	1339	1341	1342	1339	1340	1370
	[C] after treatment (mass %)	4.03	3.87	4.01	3.42	3.41	3.39
	[P] after treatment (mass %)	0.012	0.010	0.018	0.016	0.020	0.025
	Addition or not of CaF_2	None	None	None	None	None	None

(continued)

		Invention example 1	Invention example 2	Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4
Decarburization furnace	Initial [C] (mass %)	4.03	3.87	4.01	3.42	3.41	3.39
	Initial [Mn] (mass %)	0.100	0.101	0.097	0.102	0.101	0.098
	Carbonaceous material unit consumption (kg/t)	0	0	0	14.2	0	0
	Slag volume (kg/t)	20	20	30	35	40	40
	Mn ore unit consumption (kg/t)	10	10	10	10	0	5
	Blow-end Temperature (°C)	1689	1684	1687	1690	1688	1683
	Blow-end [C] (mass %)	0.451	0.448	0.450	0.449	0.448	0.447
	Blow-end [P] (mass %)	0.012	0.010	0.012	0.011	0.012	0.013
	Blow-end [Mn] (mass %)	0.384	0.381	0.305	0.282	0.100	0.178
	Mn yield (%)	71	70	52	45	-	40
	CaF_2 unit consumption (kg/t)	None	None	2	2	5	5

[0033] All the pretreatment end temperatures were aimed at 1,340°C except that of the comparative example 4 which was aimed at 1,370°C, 30°C higher than the others. Each of the pretreatment end temperatures was adjusted by controlling the charge amount per unit of iron ore injected from above during the pretreatment. Note that, if iron ore is charged before or immediately after the commencement of dephosphorizing reaction, the formation of dephosphorizing slag deteriorates due to the lowering of a molten iron temperature and therefore it is preferable to charge iron ore as late as possible in the dephosphorizing reaction period. In the decarburization treatment, when a heat margin existed, an Mn ferroalloy unit consumption was trimmed by adding Mn ore.

[0034] In the case of the invention example 1, during the desiliconizing reaction period, molten iron was desiliconized only by top-blown oxygen and a carbon source was injected over the entire desiliconizing reaction period. At the dephosphorizing reaction period, the mixture of burnt lime powder and sinter dust was injected as a flux for dephosphorization. In the case of the invention example 2, the injection of a carbon source was completed before an [Si] concentration lowered to 0.15 mass % and the mixture of burnt lime powder and sinter dust was injected from the time when the [Si] concentration lowered to 0.15 mass % to the end of dephosphorization. The other conditions are the same as those of the invention example 1.

[0035] In the case of the comparative example 1, at the desiliconizing reaction period, a carbon source and sinter dust were injected by bottom blowing and both the top-blown oxygen and the sinter dust were used as the oxygen source for desiliconization. During the dephosphorizing reaction period, the mixture of burnt lime powder and sinter dust was injected as a flux for dephosphorization. In the case of the comparative example 2, carbon source injection during the desiliconizing reaction period in molten iron pretreatment was not applied and, instead of that, lump anthracite was charged from above during decarburization treatment. Here, it is estimated that, when a carbon source is charged by the injection through the bottom-blowing nozzles during decarburization treatment, the blow-end temperature at the time of decarburization treatment rises and, as a result the service life of the bottom-blowing nozzles shortens and the cost increases. For this reason, the method of charging anthracite from above was adopted. In this case, for securing the same increased amount of [C] in molten iron as that in the cases of the invention example 1 and the comparative example 1, it was necessary to charge twice as much carbon source as that injected by a blowing method. The other conditions were the same as those of the comparative example 1. In the case of the comparative example 3, a flux and the like were not injected during molten iron pretreatment and molten iron was desiliconized by using only top-blown oxygen gas as the oxygen source and dephosphorizing slag was formed by charging burnt lime from above at the start of the pretreatment. In the case of the comparative example 4, the conditions were the same as those in the case of the comparative example 3 except that the target pretreatment end temperature was 1,370°C, 30°C higher than that of the comparative example 3.

[0036] Firstly, with regard to the phenomena at the desiliconizing reaction period, the invention example 1 and the comparative examples 1 and 2 are compared with each other. In the case of the comparative example 2, oxygen gas top blowing and sinter dust injection were applied at the desiliconizing reaction period. The iron oxide in the injected sinter dust oxidized [Si] in molten iron and also partially oxidized [C] in molten iron and CO gas was generated. Any of the reactions with iron oxide was endothermic reaction and caused the molten iron temperature to lower at the end of the desiliconizing reaction. Further, the [C] concentration in the molten iron also lowered.

[0037] In the case of the comparative example 1, [Si] and [C] in molten iron reacted with iron oxide in sinter dust in the same way as the comparative example 2 and the reaction was endothermic reaction. Further, in the comparative example 1, as the carbon source was injected at the desiliconizing reaction period, [C] in the molten iron was always maintained at a saturated level. As the reaction between [C] and iron oxide advances as a [C] concentration increases, the reaction between [C] and iron oxide advanced and the temperature at the desiliconizing reaction period lowered in the comparative example 1 more than in the comparative example 2. Further, as [C] in molten iron was maintained in a saturated state, FeO in slag tended to be reduced and $FeO-SiO_2$ slag having a low FeO concentration and a high SiO_2 concentration was formed. As a result, phenomena such as the rise of the melting point of slag and the resultant deterioration of the slag formation appeared.

[0038] In the case of the invention example 1, sinter dust was not injected at the desiliconizing reaction period and the desiliconizing reaction was advanced only by the top-blown oxygen gas. As the reaction between [Si] in molten iron and the oxygen gas was exothermic reaction, a calorific value in the invention example 1 was larger than those of the comparative examples 1 and 2 and therefore it was possible to raise the molten iron temperature at the end of the desiliconizing reaction.

In the same way as the comparative example 1, FeO in slag was likely to be reduced since [C] was maintained in a saturated state by the injection of the carbon source. However, as the amount of the top-blown oxygen gas was larger than that in the case of the comparative example 1, the amount of FeO formed by the top-blown oxygen gas was large and the slag could be maintained in the state of $FeO-SiO_2$ slag having a low melting point. For the above reasons, in the invention example 1, it was possible to make slag have a good slag formation property and to advance the succeeding dephosphorizing reaction advantageously.

[0039] Next, the state of dephosphorizing reaction in each of the examples is explained hereunder.

[0040] In the case of the invention example 1, as molten iron was desiliconized by only the top-blown oxygen without the injection of an iron oxide contained flux at the desiliconizing reaction period, the molten iron temperature at the start of the dephosphorizing reaction was high. Further, as the dephosphorizing flux added at the dephosphorizing reaction period was charged not from above but injected together with the carrier gas in molten iron, it was possible to advance a good dephosphorizing reaction without the use of fluorite by the synergistic effect with the rise of the molten iron temperature. Further, since the carbon source and the dephosphorizing flux were injected at times different from each other, there is no chance for the injected carbon source to hinder dephosphorization. Furthermore, since the temperature at the end of molten iron pretreatment was suppressed to 1,339°C, the [P] concentration after the treatment could be lowered to 0.012 mass %. Therefore, an additional dephosphorization was not necessary at the succeeding decarburization treatment and the decarburization treatment was applied by forming slag of 20 kg/t for the purpose of decreasing dust. Since the addition of fluorite could be avoided, there was no fear of fluorine elution from slag and the slag could be used effectively.

[0041] In the case of the invention example 2, in addition to the conditions in the case of the invention example 1, the carbon source injection was completed by the time the [Si] concentration lowered to 0.15 mass % and the injection of the dephosphorizing flux was started. Therefore, it was made possible to advance the dephosphorizing reaction even at the last half of the desiliconizing reaction and to accelerate the dephosphorizing reaction over the whole pretreatment. As a result, the [P] concentration after the pretreatment could be lowered to 0.010 mass %. In the meantime, since the carbon source injection time was short, the injected carbon source amount per unit was as low as a half of the invention example 1.

[0042] In the case of the comparative example 1, as sinter dust was injected and used as an oxygen source for desiliconization, the molten iron temperature at the start of dephosphorization was not sufficiently raised and the [P] concentration after the pretreatment was lowered only to 0.018 mass %. Therefore, additional dephosphorizing treatment was applied with the slag amount at the decarburization treatment controlled to 30 kg/t and further fluorite of 2 kg/t added.

[0043] In the case of the comparative example 2, as the carbon source injection was not applied during desiliconization in contrast to the comparative example 1, the [P] concentration after the pretreatment was 0.016 mass %, somewhat preferable to the case of the comparative example 1. This was because the oxygen potential could be raised because carbon source injection was not applied. On the other hand, since SiO_2 was introduced from anthracite charged at the decarburization treatment, it was necessary to increase the slag amount to 35 kg/t to secure the basicity of the slag.

[0044] In the case of the comparative example 3, as dephosphorizing slag was not injected but added from above, the [P] concentration after the pretreatment was lowered only to 0.020 mass %. Therefore, additional dephosphorizing treatment was applied with the slag amount at the decarburization treatment controlled to 40 kg/t and further fluorite of 5 kg/t added.

[0045] In the case of the comparative example 4, as the temperature after the pretreatment was controlled to a high temperature of 1,370°C in comparison with the comparative example 3, the [P] concentration after the pretreatment was 0.025 mass %, the highest of all. Therefore, additional dephosphorizing treatment was applied with the slag amount at the decarburization treatment controlled to 40 kg/t and further fluorite of 5 kg/t added.

[0046] The states of heat margin improvement and the results of the Mn ore addition in each of the examples are explained hereunder.

[0047] In the cases of the invention examples 1 and 2 and the comparative examples 1 and 2, as a result of the addition of the carbon source at the molten iron pretreatment or at the decarburization treatment, the heat margin was improved and the addition amount of Mn ferroalloy could be reduced by charging Mn ore of 10 kg/t at the decarburization treatment. In the cases of the invention examples 1 and 2, as the amount of the slag formed at the decarburization treatment could be minimized, the Mn yield of Mn ore was around 70% and thus a good result could be obtained.

[0048] In contrast, in the case of the comparative example 3, as carbon source addition was not applied, the heat margin was insufficient and Mn ore could not be added. Further, in the case of the comparative example 4, though it was attempted to increase heat margin by raising the pretreatment end temperature, a large amount of slag was formed at the decarburization treatment, as a result the heat margin decreased, and the maximum amount of Mn ore that could be added was only 5 kg/t.

[0049] The above results are summarized as follows; in the invention examples 1 and 2, as a solid oxygen source was not used at desiliconization and a flux injected into molten iron was used for dephosphorization, a high dephosphorizing capability could be obtained at the pretreatment. Further, as the carbon source was injected at a time before and different from the injection of the dephosphorizing flux during the desiliconization, it was possible to add carbon to molten iron at a high yield and to increase the heat margin at refining without the deterioration of the dephosphorizing capability.

[0050] Operations of 20 consecutive charges were carried out under the conditions of each of the invention example 1 and the comparative example 3 and the amounts of erosion of the refractories were compared with each other. As a result, it was confirmed that the refractory erosion amount of the decarburization furnace in the invention example 1 that did not use fluorite was by 30% smaller than that in the comparative example 3 that used fluorite of 5 kg/t and the invention example 1 was effective for the reduction of a refractory cost.

Industrial Applicability

[0051] The present invention, in a molten iron refining method wherein molten iron is subjected to decarburization treatment after being subjected to molten iron pretreatment wherein the molten iron is desiliconized and dephosphorized by using a refining vessel capable of top and bottom blowing, makes it possible to increase the heat margin at the refining by adding carbon to the molten iron at a high yield and, further, to obtain a high dephosphorizing capability at the pretreatment as the molten iron is desiliconized by using top-blown gas oxygen, a carbon source is injected into the molten iron during the desiliconizing reaction and, thereafter, a dephosphorizing flux is injected.

[0052] In the present invention, by starting the injection of a dephosphorizing flux after an [Si] concentration has lowered to 0.15 mass %, it is made possible to induce a dephosphorizing reaction even during a desiliconizing reaction period and to enhance the dephosphorizing capability in the pretreatment.

[0053] In the present invention, by starting the injection of a dephosphorizing flux after carbon source injection, it is made possible to increase the heat margin at refining by adding carbon to molten iron at a high yield without the deterioration of the dephosphorizing capability and to avoid the risk of ignition.

[0054] In the present invention, as a result of the improvement of the dephosphorizing capability at molten iron pretreatment, it is made possible to refine molten iron without the use of fluorite at the molten iron pretreatment and also the decarburization treatment. By so doing, the present invention makes it possible to reduce a refractory erosion amount and, thus, the refractory cost.

Claims

1. A molten iron pretreatment method wherein molten iron is desiliconized and dephosphorized by using a refining vessel capable of top and bottom blowing and injecting a flux mainly composed of a component consisting of iron oxide and optionally one or both of burnt lime and limestone through a bottom blown nozzle into the molten iron, and blowing oxygen gas into the molten iron **characterized by** injecting a carbon source through a bottom blown nozzle into the molten iron during desiliconizing reaction, desiliconizing the molten iron using top- blown oxygen gas and starting the carbon source injection prior to the commencement of said flux injection.

2. A molten iron pretreatment method according to claim 1, **characterized by** starting said flux injection after an [Si] concentration is lowered to 0.15 mass %.

3. A molten iron pretreatment method according to claim 1 or 2, **characterized by** starting said flux injection after the completion of the carbon source injection.

4. A molten iron pretreatment method according to any one of claims 1 to 3, **characterized by** not using fluorite during the molten iron pretreatment.

5. A molten iron refining method wherein molten iron is subjected to decarburization treatment after being subjected to molten iron pretreatment by the molten iron pretreatment method according to any one of claims 1 to 4, **characterized by** not using fluorite during said decarburization treatment.

Patentansprüche

1. Verfahren zur Vorbehandlung einer Eisenschmelze, wobei die Eisenschmelze entsiliziert und entphosphort wird durch die Verwendung eines Frischgefäßes, das zum Auf- und Bodenblasen imstande ist, wobei ein Flussmittel, das hauptsächlich aus einer Komponente besteht, die aus Eisenoxid und optional aus gebranntem Kalk und/oder Kalkstein besteht, durch eine Bodenblasdüse in die Eisenschmelze eingespritzt und Sauerstoffgas in die Eisenschmelze eingeblasen wird, **gekennzeichnet durch** Einspritzen einer Kohlenstoffquelle durch eine Bodenblasdüse in die Eisenschmelze während der Desilizierungsreaktion, Desilizieren der Eisenschmelze mittels aufgeblasenem Sauerstoffgas und Beginnen der Kohlenstoffquelleneinspritzung vor dem Beginn der Flussmitteleinspritzung.

2. Verfahren zur Vorbehandlung einer Eisenschmelze nach Anspruch 1, **gekennzeichnet durch** Beginnen der Flussmitteleinspritzung nachdem eine [Si]-Konzentration auf 0,15 Masse-% abgesenkt ist.

3. Verfahren zur Vorbehandlung einer Eisenschmelze nach Anspruch 1 oder 2, **gekennzeichnet durch** Beginnen der Flussmitteleinspritzung nach der Beendigung der Kohlenstoffquelleneinspritzung.

4. Verfahren zur Vorbehandlung einer Eisenschmelze nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** kein Fluorit während der Vorbehandlung der Eisenschmelze verwendet wird.

5. Verfahren zum Frischen einer Eisenschmelze, wobei die Eisenschmelze einer Entkohlungsbehandlung unterzogen wird, nachdem die Eisenschmelze einer Vorbehandlung durch das Verfahren zur Vorbehandlung einer Eisenschmelze nach einem der Ansprüche 1 bis 4 unterzogen worden ist, **dadurch gekennzeichnet, dass** kein Fluorit während der Entkohlungsbehandlung verwendet wird.

Revendications

1. Procédé de prétraitement de fer fondu, où le fer fondu est désiliconé et déphosphoré au moyen d'une cuve d'affinage permettant le soufflage par le haut et par le bas, et par injection d'un flux principalement constitué d'un composant consistant en oxyde de fer et facultativement d'oxyde de calcium et/ou de calcaire par une buse de soufflage d'air par le bas dans le fer fondu, et par soufflage d'oxygène dans le fer fondu, **caractérisé par** l'injection d'une source de carbone par une buse de soufflage d'air par le bas dans le fer fondu pendant la réaction de désiliconisation, la désiliconisation du fer fondu au moyen d'oxygène soufflé par le haut et le démarrage de l'injection de la source de carbone antérieurement à l'injection de flux.

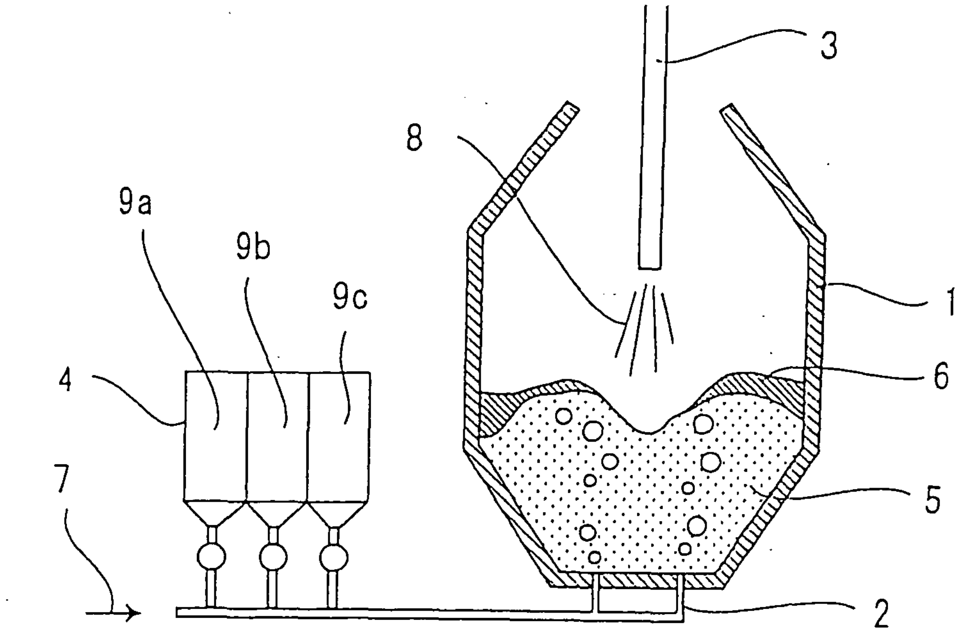
2. Procédé de prétraitement de fer fondu selon la revendication 1, **caractérisé par** le démarrage de l'injection de flux après que la concentration de [Si] a été ramenée à 0,15 % en masse.

3. Procédé de prétraitement de fer fondu selon la revendication 1 ou la revendication 2, **caractérisé par** le démarrage de l'injection de flux une fois achevée l'injection de la source de carbone.

4. Procédé de prétraitement de fer fondu selon l'une des revendications 1 à 3, **caractérisé en ce que** de la fluorite n'est pas utilisée pendant le prétraitement de fer fondu.

5. Procédé d'affinage de fer fondu, où le fer fondu est soumis à un traitement de décarburation après avoir été soumis au prétraitement de fer fondu par le procédé de prétraitement de fer fondu selon l'une des revendications 1 à 4, **caractérisé en ce que** de la fluorite n'est pas utilisée pendant le traitement de décarburation.

Fig.1



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